Electronic Supplementary Information (ESI)

Adsorption dynamics of thermoresponsive microgels with incorporated short oligo(ethylene glycol) chains at the oil-water interface

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Table S1 Reaction Compositions for the Synthesis of Microgels[*]

Microgel	Code	NIPAM: BIS: OEGMA (mol%)	NIPAM (g)	BIS (g)	OEGMA (g)
PNIPAM	MG^5	95: 5: 0	1.630	0.117	0
PNIPAM-co-MEMA	MG^5_{M10}	85: 5: 10	1.461	0.117	0.218
PNIPAM-co-DEGMA	MG^5_{D10}	85: 5: 10	1.461	0.117	0.285
PNIPAM-co-PEGMA$_{300}$	MG^5_{P10}	85: 5: 10	1.461	0.117	0.455

[*]The superscripts and subscripts in the microgel codes represent the amount of crosslinker and comonomer in mol%, respectively added during the synthesis with M = MEMA, D = DEGMA and P = PEGMA$_{300}$.
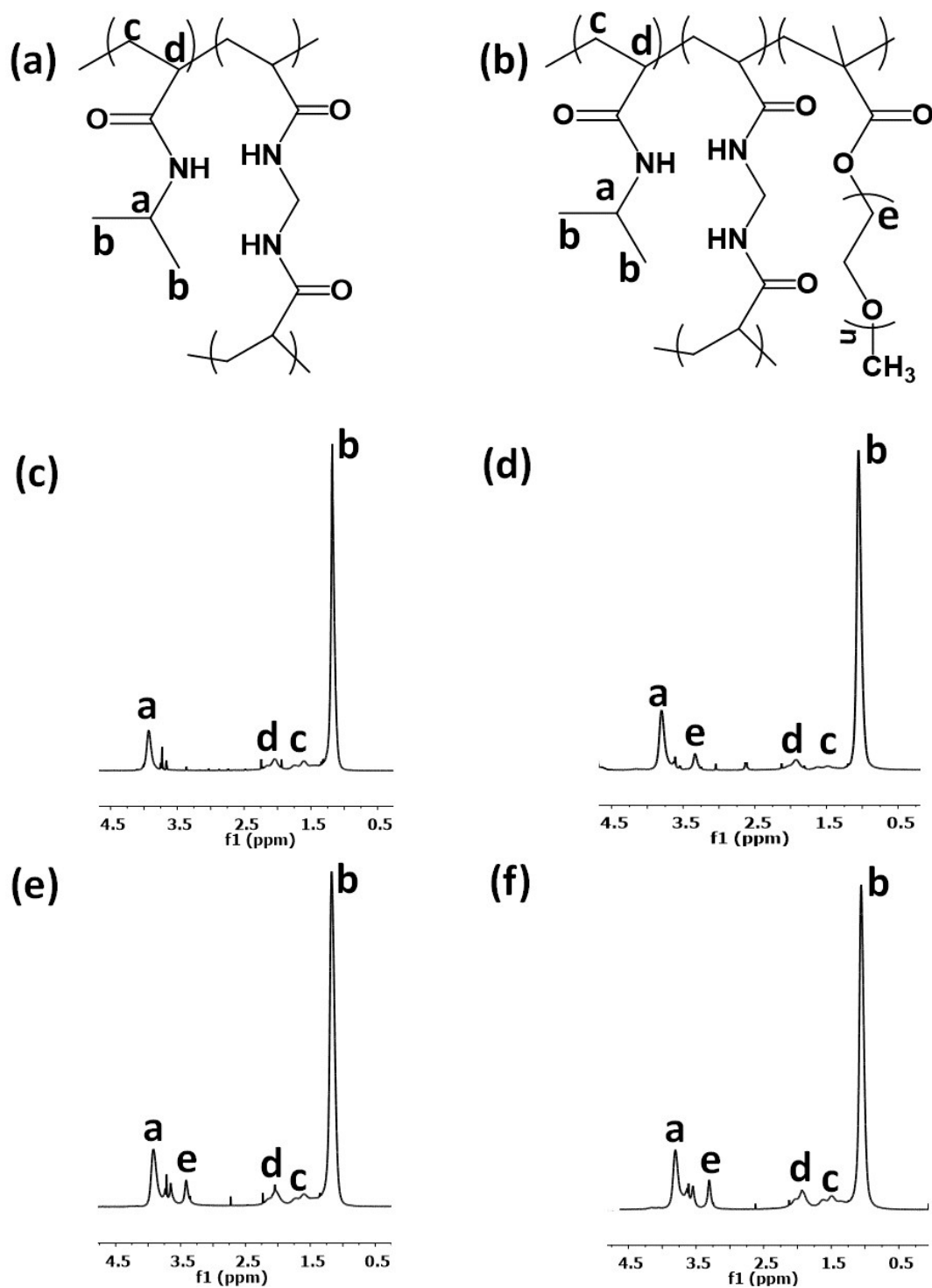
Fig. S1 Structure of (a) PNIPAM (b) functional PNIPAM microgels. ^{1}H-NMR spectra along with proton assignments for (c) pure PNIPAM, (d) PNIPAM-co-MEMA, (e) PNIPAM-co-DEGMA and (f) PNIPAM-co-PEGMA$_{300}$ microgels.
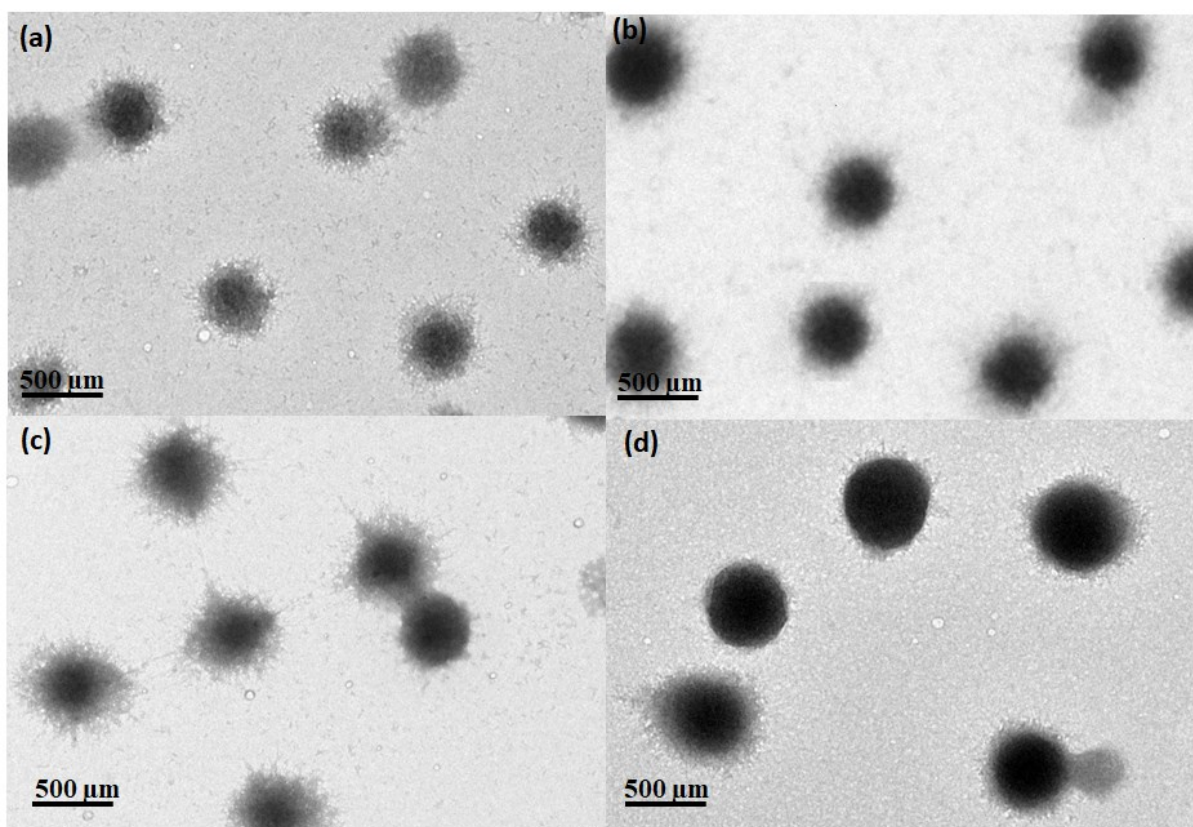
Fig. S2 TEM images of (a) pure PNIPAM, (b) PNIPAM-co-MEMA, (c) PNIPAM-co-DEGMA and (d) PNIPAM-co-PEGMA$_{300}$ microgels.
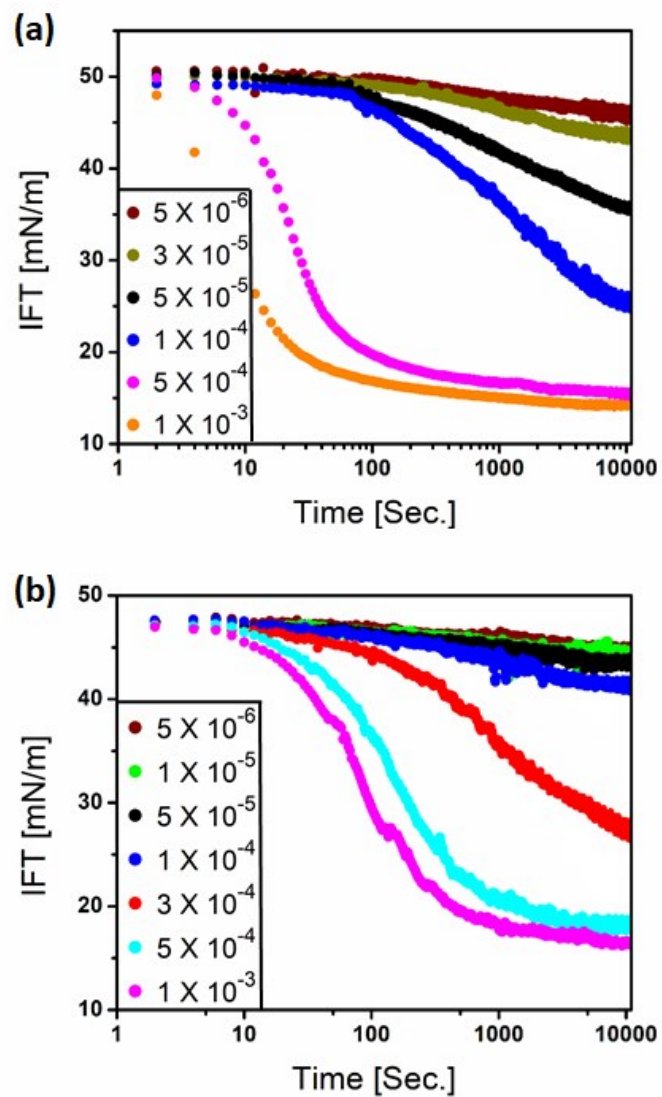
Fig. S3 Interfacial tension (IFT) of the dodecane-water interface as a function of time for the adsorption of pure PNIPAM microgels at different concentrations measured at (a) 298 and (b) 313 K. The values in the legends represent microgel concentrations in g/ml.

Determination of number concentration of microgels

The number concentrations of microgels are determined with the help of viscosity data reported in our previous work.[1] The relative viscosity (η_{rel}) of dilute microgel dispersions were measured at 298 K as a function of mass concentration using an Ubbelohde viscometer (clearance time of 320 s for 15 mL of water) immersed in a temperature-controlled water bath (accuracy ± 0.1 K). The value of η_{rel} is related to the effective volume fraction (Φ_{eff}) via Batchelor equation as follows.

$$\eta_{rel} = 1 + 2.5\Phi_{eff} + 5.9\Phi_{eff}^2 \qquad (S1)$$

Here, $\Phi_{eff} = kc$ $\qquad$ (S2)

where, k is a shift factor for converting the mass concentration to effective volume fraction and c is the concentration of microgel dispersion in wt%.

The k values are obtained from the fitting of measured η_{rel} data with eqn. (S1) as shown in Fig. S4. These values are 8.5×10^{-2}, 11.5×10^{-2}, 12.1×10^{-2} and 13.9×10^{-2} for PNIPAM, PNIPAM-co-MEMA, PNIPAM-co-DEGMA and PNIPAM-co-PEGMA$_{300}$ microgels, respectively. Then, mass of single microgel particle (m_p) is determined using the following equation.[2]

$$m_p = \frac{V_p \rho_{solvent}}{k} \qquad (S3)$$

with $V_p = \frac{4}{3}\pi R_h^3$ $\qquad$ (S4)

where, V_p is the volume of microgels, $\rho_{solvent}$ is the density of solvent and R_h is the hydrodynamic radius of microgels.

In order to estimate the mass of single microgel particle, an assumption on the microgel density in the swollen state has to be made. Further, it is assumed the density of the swollen microgel be equal to the solvent density.[3,4] The R_h values are obtained using DLS measurements. We then use the value of m_p to calculate the number concentration of microgels (N_i) in each sample

with $N_i = m_i/m_{p,i}$, where, $m_{p,i}$ and m_i are the polymer mass per microgel and the total polymer mass of the ith sample used, respectively. Note that the microgels undergo a shrinkage at temperatures above the volume phase transition temperature, while the number concentrations remain unaltered.
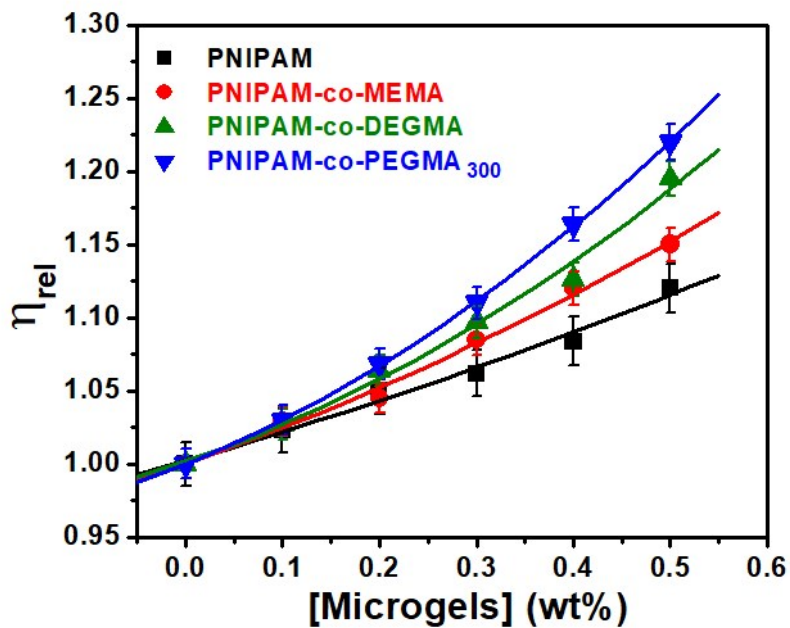

Fig. S4 Relative viscosity as a function of mass concentration of PNIPAM, PNIPAM-co-MEMA, PNIPAM-co-DEGMA and PNIPAM-co-PEGMA$_{300}$ microgels measured at 298 K. The symbols represent experimental data, the lines represent model fits of Batchelor equation.
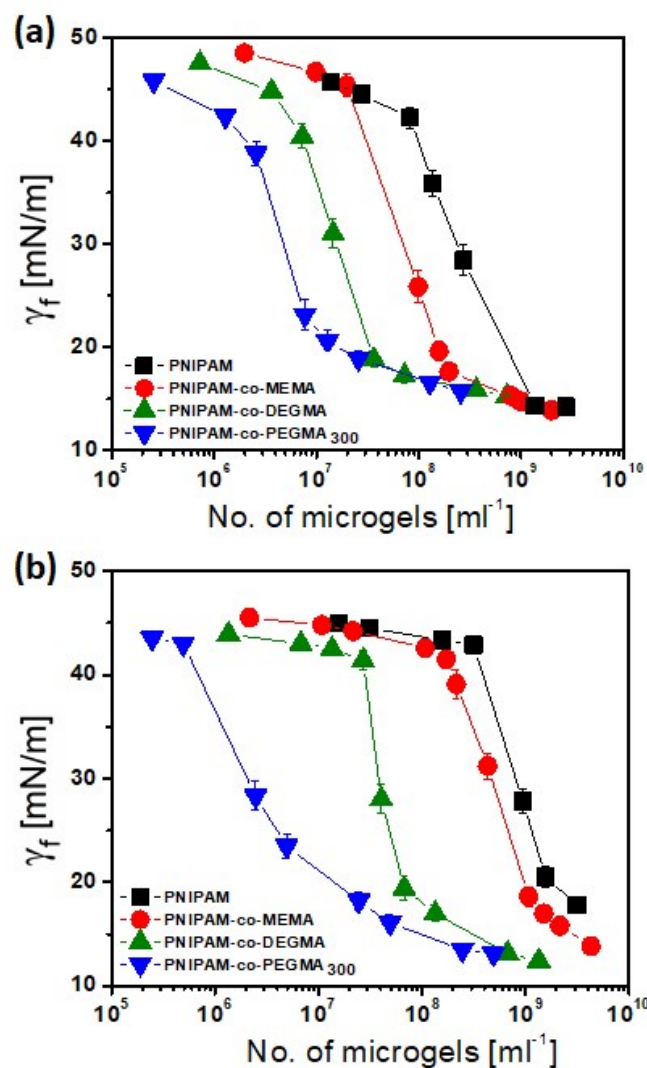
Fig. S5 Evolution of the final interfacial tension (γ_f) as a function of number concentration of pure PNIPAM, PNIPAM-co-MEMA, PNIPAM-co-DEGMA and PNIPAM-co-PEGMA$_{300}$ microgels measured at (a) 298 K and (b) 313 K. The γ_m values are obtained at 10,000 s period of time.
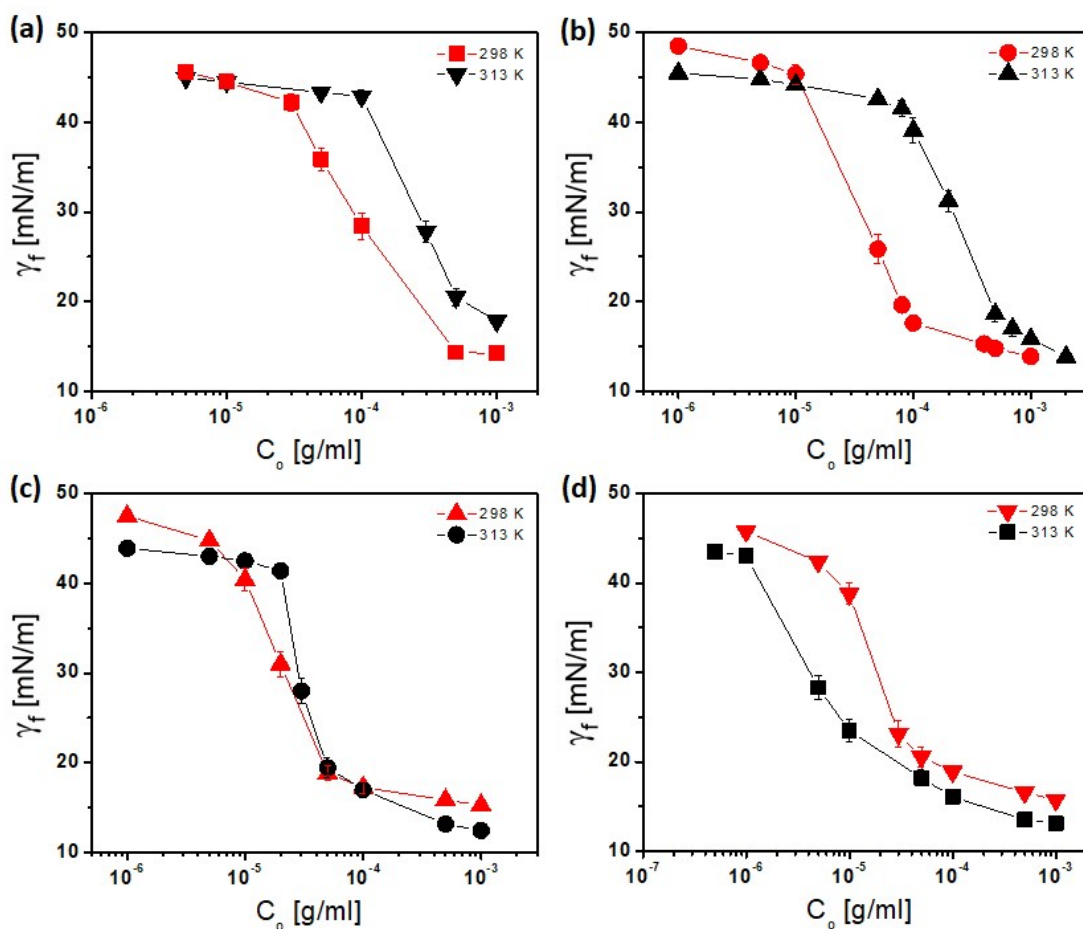
Fig. S6 Evolution of the final interfacial tension (γ_f) as a function of microgel concentration for (a) pure PNIPAM, (b) PNIPAM-co-MEMA, (c) PNIPAM-co-DEGMA and (d) PNIPAM-co-PEGMA$_{300}$ microgels at two different temperatures. The γ_m values are obtained at 10,000 s period of time.

Table S2 The values of k_i and R^2 obtained from Fig. 5 by adopting eqn. (6) at 298 K.

PNIPAM-co-MEMA	Concentration (g/ml)	5×10^{-5}	1×10^{-4}	4×10^{-4}	5×10^{-4}
	k_i (s$^{-1/2}$. mN/m)	0.1072	1.1047	4.0984	5.5838
	R^2	0.9871	0.9817	0.9904	0.9803
PNIPAM-co-DEGMA	Concentration (g/ml)	2×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}
	k_i (s$^{-1/2}$. mN/m)	0.115	0.3011	1.4385	5.5945
	R^2	0.9921	0.9878	0.9911	0.9939
PNIPAM-co-PEGMA$_{300}$	Concentration (g/ml)	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}
	k_i (s$^{-1/2}$. mN/m)	0.09	0.5726	1.2365	5.5433
	R^2	0.9887	0.9844	0.986	0.9852

Table S3 The values of k_i and R^2 obtained from Fig. 6 by adopting eqn. (6) at 313 K.

PNIPAM-co-MEMA	Concentration (g/ml)	5×10^{-5}	7×10^{-4}	1×10^{-3}	2×10^{-3}
	k_i (s$^{-1/2}$. mN/m)	0.0621	0.9273	1.7617	3.1593
	R^2	0.9848	0.9811	0.9895	0.9886
PNIPAM-co-DEGMA	Concentration (g/ml)	2×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}
	k_i (s$^{-1/2}$. mN/m)	0.0478	0.2082	0.731	4.2975
	R^2	0.9912	0.9856	0.9873	0.9917
PNIPAM-co-PEGMA$_{300}$	Concentration (g/ml)	1×10^{-5}	5×10^{-5}	1×10^{-4}	5×10^{-4}
	k_i (s$^{-1/2}$. mN/m)	0.3221	0.8705	1.9072	6.198
	R^2	0.9811	0.9759	0.9847	0.9875

References

1. P. Agnihotri, R. Raj, D. Kumar and A. Dan, *Soft Matter*, 2020, **16**, 7845–7859.

2. A. Scotti, U. Gasser, E. S. Herman, J. Han, A. Menzel, L. A. Lyon, and A. Fernandez-Nieves, *Phys. Rev. E*, 2017, **96**, 032609.

3. A. Scotti, U. Gasser, E. S. Herman, M. Pelaez-Fernandez, J. Han, A. Menzel, L. A. Lyon, and A. Fernández-Nieves, *Proc. Natl. Acad. Sci.* U. S. A., 2016, **113**, 5576–5581.

4. G. Romeo, L. Imperiali, J.-W. Kim, A. Fernández-Nieves, and D. A. Weitz, *J. Chem. Phys.*, 2012, **136**, 124905.